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Electrocatalysis at nanometer and sub-nanometer scales:
Hydrogen evolution on supported MoS₂ and Mo₃S₄ clusters

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Clean, alternative energy carriers will be needed as fossil fuel reserves are depleted. One possible energy carrier under consideration is H₂, which can be produced cleanly and renewably if solar or wind energy is coupled to water electrolysis. Unfortunately, the hydrogen evolution reaction (HER) is catalyzed most effectively by Pt group metals¹ – materials that are expensive and scarce. New materials are needed if this scheme is to ever become viable.

Having studied different metal surfaces and enzymes that catalyze hydrogen evolution, we have found a necessary criterion, a “descriptor”, for high catalytic activity – the binding energy (Gibbs free energy) of atomic hydrogen adsorption must be close to zero.^{1,2} Not surprisingly, the nitrogenase and hydrogenase enzymes – both of which evolve H₂ in nature – satisfy this requirement. In an effort to develop solid-state analogues of the enzymatic active sites, theoretical calculations have guided us to MoS₂ nanoparticles and Mo₃S₄ complexes, which were subsequently synthesized and investigated for hydrogen evolution.

Having already confirmed the catalytic activity of MoS₂ nanoparticles for hydrogen evolution², more recently we have aimed to identify relationships between structure and catalytic activity within the MoS₂ nanoparticles. In our approach, we combine ultra high vacuum techniques with electrochemical measurements under ambient conditions. MoS₂ nanoparticles were first synthesized on Au(111) in ultra-high vacuum, where scanning tunnelling microscopy (STM) was used to investigate their structure, morphology, and surface coverage (Fig. 1). Surface spectroscopy was also employed for chemical characterization. These UHV-prepared samples were then transferred to an electrochemical cell where catalytic activity for hydrogen evolution was measured. By varying particle size and coverage within the sample set, our measurements have established – for the first time – a clear relationship between the structure and catalytic activity of MoS₂ nanoparticles.

Bearing in mind the active edge state in MoS₂ nanoparticles², we have looked to other solid-state systems which also mimic the active site within nitrogenase and/or hydrogenase. One candidate material

is an aquo, tri-nuclear molybdenum complex, [Mo₃S₄]⁴⁺, which we have synthesized following the procedure in reference 3 (see Fig. 2). Our theoretical model predicts these complexes to be active for hydrogen evolution, and to investigate them experimentally we have deposited them as individual, separate entities onto an inert HOPG substrate. We subsequently characterized these catalysts using STM, surface spectroscopy, and electrochemical methods. The supported Mo₃S₄ complexes demonstrated excellent catalytic activity for hydrogen evolution, just below that of the Pt-group metals, per active site.

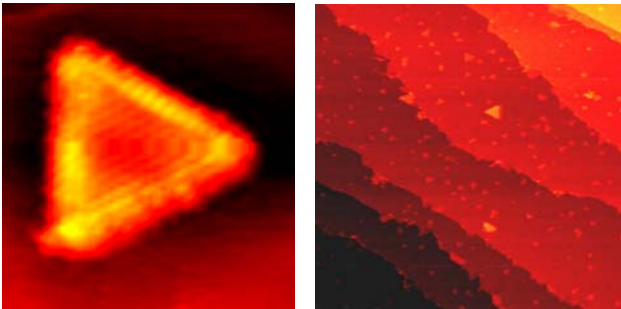


Fig. 1. STM images (width 7 nm and 150 nm) of MoS₂ nanoparticles on Au(111).

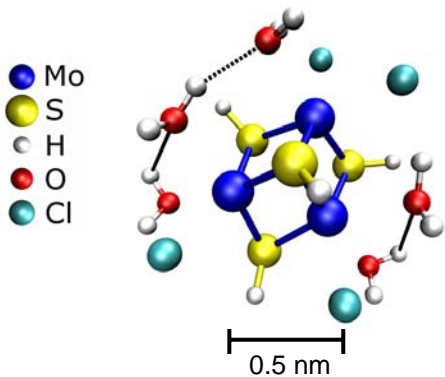


Fig. 2. DFT-calculated structure of the protonated [Mo₃S₄]⁴⁺ complex in aq. HCl.

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